



Formation of 1-cyclopenten-1-ylmethanol from the reaction of excess allylmagnesium chloride with propargyl alcohol.

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This compound, was a byproduct of the reaction of excess allyl magnesium chloride with the internal alkyn carbon of propargyl alcohol, yielding 2-methylene-4-penten-1-ol¹. This compound is postulated to arise from intra molecular cyclo addition of an intermediate vinyl carbanion to the terminal vinyl group of the intermediate, followed by hydrolysis.

Anal. Calcd. for C₆H₁₀O : C, 73.43 ; H, 10.27.

Found: C, 73.29 ; H, 10.44.

b.p.188-90° , n_D²⁷ 1.4767

The infrared spectrum (neat) showed bands at 3400 (s), 3030 (w), 2900 (s), 2850 (s), 1650 (w), 1440 (m), 1420 (m), 1360 (w), 1320(w), 1300 (w), 1265 (w), 1220(w), 1100 (w), 1150(w), 1045 (s), 10150 (m), 985(m), 950(w), 935(w), 905 (w), and 825(w), cm⁻¹.

The pmr spectrum (60MHz), CDCl₃, showed a multiplet at δ2.20 (6H, aliphatics), a broad singlet at 3.95 (1H, hydroxyl, collapses on addition of D₂O), a multiplet centered at 4.15 (2H, deshielded aliphatics), and a multiplet centered at 5.60 (1H, internal olefinic).

The ultraviolet spectrum showed only end absorption above 210 mu.

Catalytic hydrogenation of the compound gave a 139% hydrogen absorption of that theoretical for saturating one double bond and yielded a saturated aldehyde as the major product, due to the now well documented ² hydrogen transfer reaction of allylic alcohols on palladium catalysts. Treatment of the compound with 2,4-dinitrophenylhydrazine reagent by the procedure of Shriner and Fuson ³ gave yellow powder. Recrystallization from ethanol/water gave yellow crystals, m.p. 159-161°, lit: ⁴, m.p. 159.5-160°.

References:

1. John H. MacMillan and Alfred Viola,

"Addition of unsaturated propargyl, allyl and benzyl Grignard Reagents to acetylenic or allylic alcohols.", internet archive, 2012.

http://www.ccl.net/cca/documents/MacMillan_Papers/Addition_of_propargyl_allyl_and_benzyl_Grignard_reagents_to_alpha_beta_unsaturated_alcohols.pdf

2. J. Wiemann and G. Laude, C. R. Acad. Sci. Paris, 226, 345, (1948).

3. P. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds", 5th ed., John Wiley and Sons, Inc., New York, N. Y., 1964.

4. <http://chemyq.com/En/xz/xz3/28128hhqo.htm>